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A New Method of Silane Coupling Treatment: Chemical Surface Modifications of Metal Oxides with Hydrosilane

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Chemical surface modifications of Al_2O_3, TiO_2, and SiO_2 by using diphenylsilane bearing hydrosilyl moieties were investigated by IR spectroscopy and gas chromatography. The hydrosilane was observed to adsorb on the metal oxide surfaces by forming Si–O–metal bonds with generation of hydrogen gas. The results show that hydrosilanes can be used as chemical surface modifiers such as the usual silane coupling agents of silanols, chlorosilanes, and alkoxysilanes.

Organosilicon compounds such as silanols $[R_{4-n}Si(OH)_n]$, chlorosilanes $(R_{4-n}SiCl_n)$, and alkoxysilanes $[R_{4-n}Si(OR')_n$; $R' = Me, Et]$ are well known to have high bonding ability to various metal oxide surfaces by forming Si–O–metal bonds,[1] and the chemical surface modifications of metal oxides by using those compounds are commonly called silane coupling treatment.[1,2] The treatments give functional properties to the metal oxide surfaces of molecular-selective adsorption, light-absorption, water repellence, adhesive properties to organic compounds, and so on, and are generally used to produce organic–inorganic hybrid materials.[1–3] However, those organosilicon compounds are usually highly reactive toward decomposition by hydrolysis and intermolecular condensation and can be hardly handled under humid conditions.[2,3] There are also difficulties in refining them by using column chromatography due to their chemical adsorption to the packed metal oxide materials.[2,4]

On the other hand, hydrosilanes $(R_{4-n}SiH_n)$, which are usually more stable and can be handled much easier than silanols, chlorosilanes, and alkoxysilanes, have been reported to react on titania (TiO_2) surface with formation of Si–O–Ti bonds.[5] This fact indicates that hydrosilanes have potential as chemical surface modifiers. However, the reactivity of hydrosilanes to metal oxides other than TiO_2 and the reaction mechanisms have not been clarified yet. In this work, we selected diphenylsilane as a model compound and examined the potential of the hydrosilane as the silane coupling agent to form Si–O–metal bonds on the surfaces of the metal oxides of alumina (Al_2O_3), TiO_2, and silica (SiO_2) by IR spectroscopy and gas chromatography.

Three kinds of commercially available metal oxide ultrafine powders were used in this work: Al_2O_3 (AEROXIDE Alu C), which has a primary particle size of ca. 13 nm, was purchased from Nippon Aerosil; TiO_2 (ST-21), which has a primary particle size of ca. 20 nm, was purchased from Ishihara Sangyo; and SiO_2 (AEROSIL 90G), which has a primary particle size of ca. 20 nm, was purchased from Nippon Aerosil. Chemical surface modifications of the metal oxide powders were examined by immersion: the metal oxide powders as received were immersed in a 10 mM cyclohexane solution of diphenylsilane (Tokyo Chemical Industry) for 15 h at 65 °C. The surface-modified metal oxide samples were collected from the solution by centrifugation, then washed in methanol or acetonitrile and dried at room temperature. The IR absorption spectra of the surface-modified metal oxide samples and diphenylsilane were measured at 25 °C with a Nicolet MAGNA-IR560 spectrometer. The measurements were performed for the samples mixed with KBr powder by diffuse reflectance, and the spectra were recorded with 640 scans in the range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. In order to obtain information about the reaction of diphenylsilane on the metal oxide surfaces, the generated gas by the reaction was analyzed by the use of a Shimadzu GC-8A gas chromatograph with an Ar carrier gas.

Figure 1 shows the normalized IR absorption spectra of the surface-modified Al_2O_3, TiO_2, and SiO_2 powder samples (a–c), and diphenylsilane (d) in the energy region from 3800 to 2950 cm^{-1} and from 2250 to 2050 cm^{-1}. All the surface-modified metal oxide samples showed a broad absorption spreading over the energy region between 3750 and 2950 cm^{-1}. The broad absorption is attributable to the O–H stretching vibrations of the hydroxy groups existing on the metal oxide surfaces and those of the water adsorbed on the surfaces of the metal oxides.[6] Besides the broad absorption, all the samples exhibited characteristic absorption bands due to the aromatic C–H stretching vibrations in the phenyl groups at around 3070 cm^{-1} as observed in diphenylsilane.[7] The results indicate that diphenylsilane possesses bonding ability to metal oxide surfaces of Al_2O_3, TiO_2, and SiO_2. The adsorbed amounts of diphenylsilane were estimated from the IR absorption intensities to be 0.6 for Al_2O_3, 1.1 for TiO_2, and 0.1 for SiO_2, respectively, in comparison with the case of the conventional analog of diphenyldimethoxysilane.

In addition to the IR spectroscopic data, generations of hydrogen gas (H_2) were confirmed by gas chromatography in the reactions of diphenylsilane on the metal oxide surfaces for all the cases of Al_2O_3, TiO_2, and SiO_2. From these results, diphenylsilane is considered to adsorb on the metal oxide surfaces by forming Si–O–metal (metal: Al, Ti, and Si) bonds similar to the typical silane coupling agents of silanols, chlorosilanes, and alkoxysilanes through the reaction shown in Figure 2. Since the electronegativity of Si ($\chi_{Si} = 1.90$) is lower than that of H ($\chi_H = 2.20$),[8] the negatively charged oxygen of the hydroxy group on the metal oxide surface coordinates to the positively charged Si of the hydrosilyl moiety (Si–H) and then direct condensation reaction proceeds as the dehydrogenation

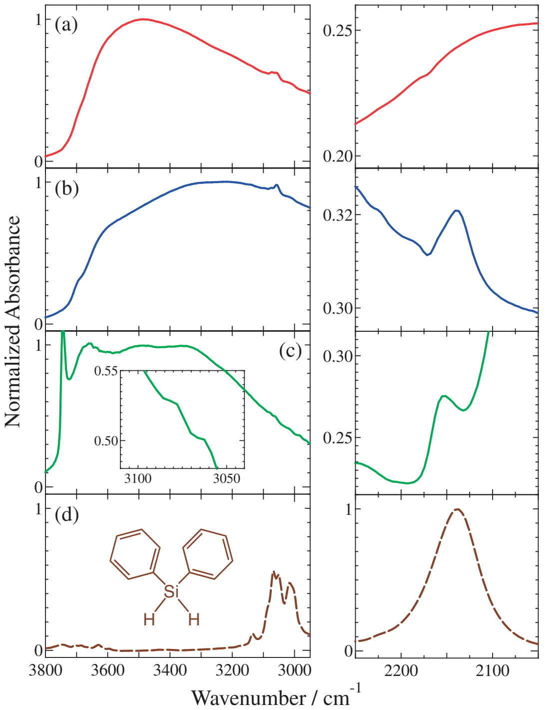

Figure 1. Normalized IR absorption spectra of chemically surface-modified metal oxide powder samples by diphenylsilane in the energy region from 3800 to 2950 cm^{-1} and from 2250 to 2050 cm^{-1}; (a) Al_2O_3, (b) TiO_2, and (c) SiO_2. IR spectra of diphenylsilane are also shown in (d).

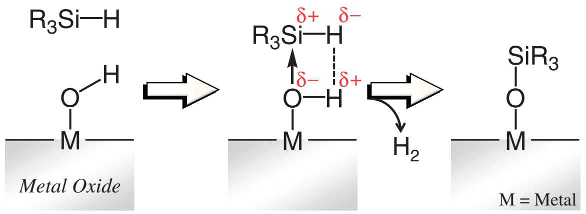

Figure 2. Mechanism of the formation of the Si–O–metal bond in the reaction between a hydrosilyl moiety and a hydroxy group on the metal oxide surface.

reaction of the hydrosilane with the formation of the Si–O–metal bond.

On the other hand, no characteristic absorption due to the Si–H stretching vibration in the hydrosilyl moiety at around 2150 cm^{-1} was observed in the IR spectrum of the chemically surface-modified Al_2O_3 powder sample (Figure 1a).[7] The result indicates that the two hydrosilyl moieties of diphenylsilane are used in the dehydrogenation reaction of the chemical surface modification for the Al_2O_3 powder. In contrast to that, the chemically surface-modified TiO_2 and SiO_2 powder samples showed the IR absorption band attributable to the hydrosilyl moiety at around 2150 cm^{-1} (Figures 1b and 1c), indicating that not all the hydrosilyl moieties participate in the surface modification reactions. The difference in the bonding structures is considered to be due to the difference in the areal densities of hydroxy groups on the surfaces of metal oxides.[6a,6c,9]

In this study, we examined the reactivity of diphenylsilane to the surfaces of the various metal oxides (Al_2O_3, TiO_2, and SiO_2), and found that the hydrosilyl moiety works as a functional group to form a Si–O–metal bond, and thus hydrosilanes can be used as the chemical surface modifiers of metal oxides. Hydrosilanes have an advantage of ease of synthesis, purification, and handling over commonly used silane coupling agents such as silanols, chlorosilanes, and alkoxysilanes, which extends the degree of freedom of the molecular design of the chemical surface modifiers. Therefore, we believe that the modification reaction using hydrosilane is important as a new method of covalent attachment of organic moieties on the surfaces of metal oxides.

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